Temperature and moisture dependence of soil H_2 uptake measured in the laboratory

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Received 28 April 2006; revised 2 June 2006; accepted 13 June 2006; published 25 July 2006.

[1] The soil sink of molecular hydrogen is the largest and most uncertain term in the global atmospheric H_2 budget. Lack of information about the mechanisms regulating this sink limits our ability to predict how atmospheric H_2 may respond to future changes in climate or anthropogenic emissions. Here we present the results from a series of laboratory experiments designed to systematically evaluate and describe the temperature and soil moisture dependence of H_2 uptake by soils from boreal forest and desert ecosystems. We observed substantial H_2 uptake between -4°C and 0°C, a broad temperature optimum between 20°C and 30°C, a soil moisture optimum at approximately 20% saturation, and inhibition of uptake at both low and high soil moisture. A sigmoidal function described the temperature response of H_2 uptake by soils between -15°C and 40°C. Based on our results, we present a framework for a model of the soil H_2 sink. **Citation:** Smith-Downey, N. V., J. T. Randerson, and J. M. Eiler (2006), Temperature and moisture dependence of soil H_2 uptake measured in the laboratory, *Geophys. Res. Lett.*, *33*, L14813, doi:10.1029/2006GL026749.

1. Introduction

[2] Molecular hydrogen (H_2) is the second most abundant reduced gas in the troposphere (after methane), with a concentration of approximately 530 ppb during the 1990s [*Novelli et al.*, 1999]. Sources of H_2 to the troposphere include photolysis of formaldehyde, which is primarily generated from the oxidation of methane and non-methane hydrocarbons, and emissions from fossil fuel combustion and biomass burning. Sinks of hydrogen include oxidation by OH and uptake by soils [*Novelli et al.*, 1999]. The soil sink is the largest and most uncertain term in the H_2 budget. Estimating the magnitude of the soil sink has proved challenging and the calculated proportion of H_2 uptake by soils to total loss has varied from 62% to 92% [*Seiler and Conrad*, 1987; *Warneck*, 1988; *Ehhalt*, 1999; *Novelli et al.*, 1999; *Gerst and Quay*, 2001; *Hauglustaine and Ehhalt*, 2002]. The prospect of a global hydrogen economy has sparked interest in the environmental impact of substantial increases in H_2 emissions. A hydrogen economy may be accompanied by reduced NO_x emissions, which would increase the atmospheric lifetimes of CH_4 and CO due to decreases in OH, and decrease tropospheric O_3 levels in polluted urban areas [*Schultz et al.*, 2003]. *Tromp et al.* [2003] and *Warwick et al.* [2004] found that replacing fossil fuels with hydrogen fuel cells would lead to a decrease in stratospheric ozone because H_2 mixes freely across the tropopause and forms water in the stratosphere. A critical aspect of this problem is the response of the soil sink. Because neither the mechanism nor the environmental controls on soil uptake of H_2 are well defined it is difficult to predict both temporal and spatial variability in the magnitude of this sink and how it may respond to future changes in climate or anthropogenic emissions.

[3] *Schuler and Conrad* [1991] studied the temperature response of H_2 uptake by soils from a temperate forest, compost bin, and a private garden. They found that at H_2 concentrations of 1 ppm, the uptake was optimized at a temperature of 30°C whereas at higher H_2 concentrations (3000 ppm) H_2 uptake was optimized at 65°C. At 1 ppm, rates of soil H_2 uptake doubled when temperature was increased from 5°C to 30°C. In an incubation experiment that measured soil uptake for H_2 concentrations between 100 and 500 ppm, *Trevors* [1985] found a lower temperature optimum (20°C) for aerobic soils at 60% water holding capacity (WHC) and observed a 3-fold increase in uptake between 5 and 20°C. Another experiment by *Yonemura et al.* [2000b] found a similar temperature optimum, and a factor of 2 difference in uptake rate between 1°C and 25°C at a single soil moisture level.

[4] Previous work suggests that soil moisture also plays an important role in determining the uptake rate of H_2. Experiments by *Conrad and Seiler* [1981; 1985] and *Fallon* [1982] show that in very dry soils, uptake is stimulated by the addition of water. *Godde et al.* [2000] measured the H_2 oxidation capacity of soils from a temperate forest, agricultural field and meadow in Germany, and found that uptake was generally higher in drier soils (at 30% WHC) than in wetter soils (at 60% WHC). Field studies from a forest and arable field in Japan show that at high soil moisture levels (> 30% volumetric water content) H_2 uptake decreases with increasing soil moisture [*Yonemura et al.*, 1999; 2000a], probably from limited H_2 diffusion through water filled soils [*Yonemura et al.*, 2000b].

[5] Although several experiments on the temperature and moisture response of H_2 uptake by soils exist, there are insufficient data to parameterize a mechanistic model that predicts soil H_2 fluxes across the full range of environmental conditions found in Earth's major biomes. Such a model would be useful in exploring the sources of variability in the atmospheric H_2 record and could be used to predict changes in the H_2 cycle due to changing climate or emissions. To construct a mechanistic model of H_2 soil uptake, more information is needed about the interaction

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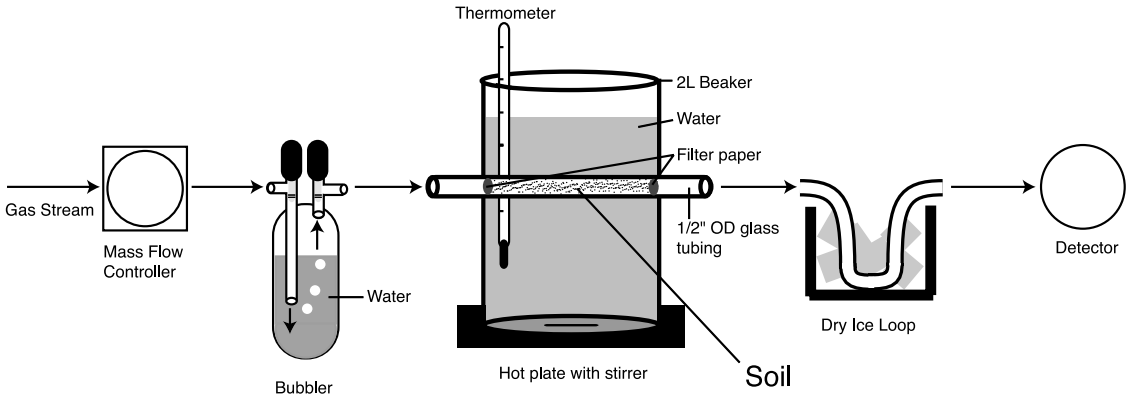

Figure 1. Experimental setup for measuring the temperature and moisture dependence of H_2 uptake by soils. Air with known [H_2] is pushed through the system from left to right and the outgoing [H_2] is measured to determine uptake in the soil column using equation (1). The bubbler hydrated the incoming gas stream slightly, which prevented desiccation of soils over the course of our experiments. The bubbler was removed from the system for the 11% saturated Mojave Desert experiment to prevent addition of water to the soil. The entire beaker apparatus was weighed both before and after each experiment to monitor changes in water content over the course of each experiment.

between soil temperature and soil moisture, the sensitivity of soil H_2 uptake to soil moisture under unsaturated conditions, rates of soil H_2 uptake at temperatures below 0°C, and differences in uptake between different biomes.

[6] We measured rates of H_2 uptake by soils across a wide range of temperatures and soil moisture levels using a flow-through chamber system. In our experiments we used two different surface soils, one from a mature black spruce boreal forest in interior Alaska and another from the Mojave Desert in California. Our experiments imply that there is 1) a strong soil temperature control on H_2 uptake, 2) a minimum soil moisture requirement for biological activation, 3) maximized uptake at approximately 20% saturation, 4) decreasing uptake at higher soil moisture levels, 5) substantial H_2 uptake occurring between −4°C and 0°C and 6) that soil type affects the shape of the moisture response. We propose a framework from which global H_2 uptake by soils can be modeled based on these data.

2. Methods

2.1. Soil Collection and Preparation

[7] Approximately 500 mL of the top 5 cm of soil was collected from a black spruce (*Piceae Mariana*) forest near Delta Junction, Alaska (63°53′N, 145°44′W) and from the University of California Burns Piñon Ecological Reserve in the Mojave Desert (34°08′N, 116°27′W). From 1961 to 1990 the mean annual temperature was −2.3°C at the boreal forest site and 20°C at the Mojave Desert site. Mean annual precipitation was 30 cm/yr at the boreal forest site and 11 cm/yr at the Mojave Desert site (Western Regional Climate Center (WRCC) station observations from Big Delta, AK and Twentynine Palms, CA, available online at http://www.wrcc.dri.edu/clim-sum.html). Soils were stored in sealed containers for transport back to the lab, after which they were stored at room temperature in jars sealed with Parafilm. The carbon and nitrogen content of the boreal forest soil was 38.5% C and 1.11% N whereas the Mojave Desert soil was 0.3% C and 0.02% N (measured with an elemental analyzer, Carlo Erba, Lakewood, NJ).

2.2. Flux Measurements

[8] Hydrogen calibration gases between 5 and 2000 ppb H_2 were generated by diluting a standard gas containing 5070 ± 25 ppm H_2 (Scott-Marrin, Riverside, CA) with ultra-pure N_2. Samples from cylinders of compressed air were measured following calibration of the instrument and these cylinders were used as secondary standards throughout the experiment.

[9] We created a flow through apparatus for measuring H_2 uptake by insetting a $\frac{1}{2}''$ OD glass tube through a 2L beaker and filling the tube with soil (Figure 1). Gas from a compressed air cylinder containing 1585 ± 21 ppb H_2 flowed, in order, through a mass flow controller (MKS, Wilmington, MA), through a flask filled with water to control humidity, through the $\frac{1}{2}''$ glass tube filled with the soil sample, through a dry ice loop to remove moisture and finally to the inlet of a TA 3000R Reducing Gas Analyzer (Ametek Process Instruments, Newark, DE) at a rate of 10 standard cubic centimeters per minute (sccm). The TA3000R RGA is a continuous flow instrument with a Unibead 1S and an MS 13X column for separation of H_2 and CO. Ultra-torr fittings (Swagelok, Solon, OH) were used at each joint, and the system was leak tested with an 80% H_2 source. The TA 3000R instrument measures H_2 with a relative precision of 1.5%.

2.3. Temperature and Moisture Experiments

[10] In preparation for the temperature and moisture manipulation experiments, soils were thinly spread out in plastic pans and allowed to dry at room temperature (23°C) overnight. Soil samples were then split into 5 equal portions and water was added to each sample in increments. In these experiments, soil moisture was described as '% saturated', which was calculated as the ratio of water (g) contained in soils to the amount contained after soils are fully submerged in pure H_2O and allowed to drain for 10 minutes. The soils were stirred to evenly incorporate the added water and stored in 50 mL test tubes sealed with Parafilm for at least 3 days before experiments began. The manipulation of the soils may have changed the soil porosity and existing

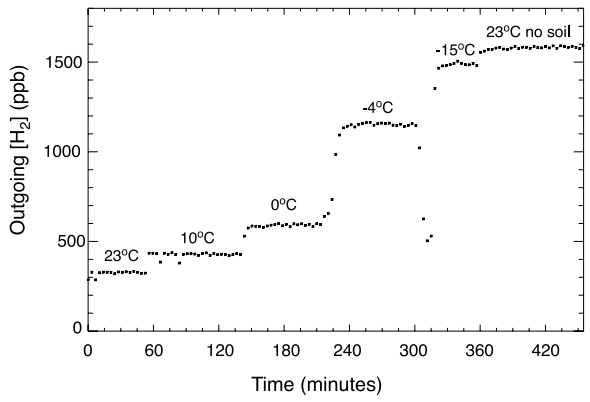

Figure 2. Time series of $[H_2]_{out}$ from a single laboratory experiment using the boreal forest soils at 23% saturation. The difference between the 23°C no soil ($[H_2]_{in}$) and $[H_2]_{out}$ was used in equation 1 to calculate the uptake of H_2 in the soil column. The drop in $[H_2]_{out}$ between −4°C and −15°C corresponds with a warm temperature excursion due to the exchange of the salt-water solution from the beaker with an ethanol/ice solution.

microbial communities and, for this reason, our results may not be representative of in situ fluxes.

[11] For each soil moisture level, the column was filled with 10 mL of soil with a cone of filter paper at each end. The beaker was filled with water of different temperatures, and the concentration of outgoing H_2 was measured every 3.5 minutes. Temperatures were cycled through in the following order 23, 30, 37, 10, 0, −4, −15°C (Figure 2). We used a hot plate to maintain 30°C and 37°C, a water bath with periodic ice additions to maintain 10°C, an ice water bath to maintain 0°C, an ice/salt water bath to maintain −4°C, and an ice/ethanol/water bath to maintain −15°C. The water in the beaker was drained and replaced between each temperature level to ensure a quick transition. We used a stir bar to avoid temperature stratification within the beaker. We conducted one set of temperature manipulations on soils with a thermocouple embedded in the soil and another in the water bath. The temperature of the soil equilibrated with the water bath temperature within minutes, and there was no observed temperature offset between the soil and the water bath. The thermocouple wire could not be placed in the soil during the flow through experiments because a gas-tight seal was necessary at each joint. Each temperature/moisture level was considered stable after the outgoing H_2 concentration had remained constant for at least 30 minutes (e.g., Figure 2).

2.4. Uptake Rate Estimates

[12] The uptake rate (pmol cm^{-3}_{soil} s^{-1}) of each soil sample was calculated using the measured difference between the incoming and outgoing H_2 concentrations:

$$H_2uptake = \frac{\left([H_2]_{in} - [H_2]_{out}\right) \cdot f \cdot P}{V_{soil} \cdot R \cdot T \cdot 1 \cdot 10^9} \quad (1)$$

where f is the flow rate (cm^3/s), P is the pressure (Pa), V_{soil} is the volume of soil (cm^3), R is the gas constant and T is the temperature (K). Pressure was assumed to be 1.01325×10^5 Pa.

3. Results

[13] Our experiments showed a dependence of H_2 uptake on soil moisture and temperature in both soils (Figure 3). The maximum flux from the boreal forest soil (0.8 pmol cm^{-3} soil s^{-1}) was approximately twice as large as the maximum flux rate from the Mojave Desert soil (0.35 pmol cm^{-3} soil s^{-1}). We observed a broad temperature maximum between 10°C and 35°C (Figure 3). Substantial uptake continued at −4°C (especially for intermediate soil moisture levels), but was nearly eliminated by −15°C. The uptake rate increased sharply with increasing temperature between −4°C and 0°C for the boreal forest soils at intermediate saturation levels, whereas the changes in uptake rate with temperature were more gradual in the Mojave Desert soils. In a similar experiment on soils from a California forest, fluxes decreased substantially when the temperature was increased to 65°C (Figure S1[1]) suggesting uptake inhibition at high temperatures.

[14] We observed both high and low soil moisture inhibition of H_2 uptake with soils from both sites (Figure 3). For the boreal forest soils, increasing the saturation level from 4% to 10% caused uptake to increase by 300% at 23°C. Similarly, increasing the saturation from 11% to 19% for the Mojave Desert soils caused the uptake rate to increase from approximately zero to the maximum uptake levels (Figure 3). The boreal forest soils continued consuming substantial H_2 at higher saturation levels than the Mojave Desert soils, and did not show evidence of moisture inhibition until 59% saturation.

[15] We constructed normalized contour plots of the boreal forest and Mojave Desert fluxes as a function of both temperature and soil moisture (Figure 4). Contour values ranged between 0 and 1 and were scaled by the maximum observed flux at each site. The maximum flux occurred at 23°C and 23% saturation for the boreal forest soil, and at 30°C and 19% saturation for the Mojave Desert soil.

[16] The response to temperature, when normalized to the maximum flux at each soil moisture level, was similar between the two sites and can be described by a sigmoidal function with the following parameters (Figure S2):

$$f(T) = \frac{1}{1 + \exp(-0.1718 \cdot T + 46.938)} \quad (2)$$

where T is the temperature (K). This function is valid for temperatures between −15°C and 40°C (with an r^2 of 0.72). At temperatures above 40°C, our results suggest that uptake decreases with increasing temperature (Figure S1).

[17] The moisture response cannot be characterized by a simple function, largely due to the effect of soil moisture on the diffusion of H_2 into soils, which varies considerably with soil type. It is clear, however, that a minimum level of soil moisture must be attained before uptake is possible. To account for the effects of soil moisture as it fills pore space,

[1] Auxiliary material is available in the HTML. doi:10.1029/2006GL026749.

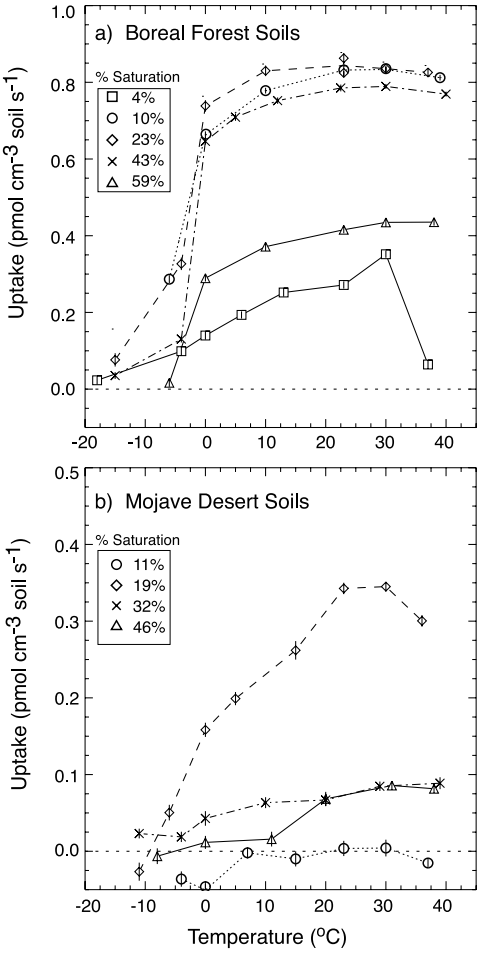

Figure 3. Hydrogen uptake rates as a function of temperature for different soil moisture levels. (a) Boreal forest soils collected near Delta Junction, AK and (b) Mojave Desert soils collected near Yucca Valley, CA. Note that the scale in Figure 3a is twice that of Figure 3b. Uptake rate at 23°C was measured twice for the boreal forest soils at 10% and 23% saturation, and in both cases the difference between measurements was less than 5%. Standard deviations were calculated as $\sqrt{\sigma_{in}^2 + \sigma_{out}^2}$ where σ_{in} and σ_{out} are the standard deviation of the measurement of incoming and outgoing $[H_2]$ respectively. The negative values observed probably do not represent an actual production of H_2, but illustrate the level of internal noise in our measurement system.

hydrogen uptake must be modeled as a diffusion process where the uptake rate is scaled according to the results presented here:

$$\lambda_s = f(T)g(M) * \lambda_{\max} * [H_2] * \frac{P}{R * T} \quad (3)$$

where $f(T)$ and $g(M)$ are functions of soil temperature (T) (Equation 2) and moisture (M) respectively that range between 0 and 1, λ_{max} is the maximum possible H_2 uptake (1/s) under ideal soil temperature and moisture conditions (i.e., when $f(T)$ and $g(M)$ are equal to 1), $[H_2]$ is the available hydrogen concentration (ppb), P is pressure (Pa), R is the gas constant, and T is temperature (K). We assumed that the reaction was first order based on chamber measurements of H_2 uptake in the field. This framework can be used to estimate H_2 uptake as a function of soil moisture and temperature.

4. Discussion and Conclusions

[18] We systematically defined the temperature and moisture controls on soil H_2 uptake over a wide range of environmental conditions and identified, for the first time, uptake at subzero temperatures (from −4°C to 0°C). Our results provide additional evidence that a minimum moisture level is required for biological activation of microbes utilizing H_2 [e.g., *Conrad and Seiler*, 1981; *Fallon*, 1982; *Conrad and Seiler*, 1985], but that once pore spaces are filled with water, diffusion of H_2 into the soil becomes limited and fluxes decrease [e.g., *Yonemura et al.*, 2000b].

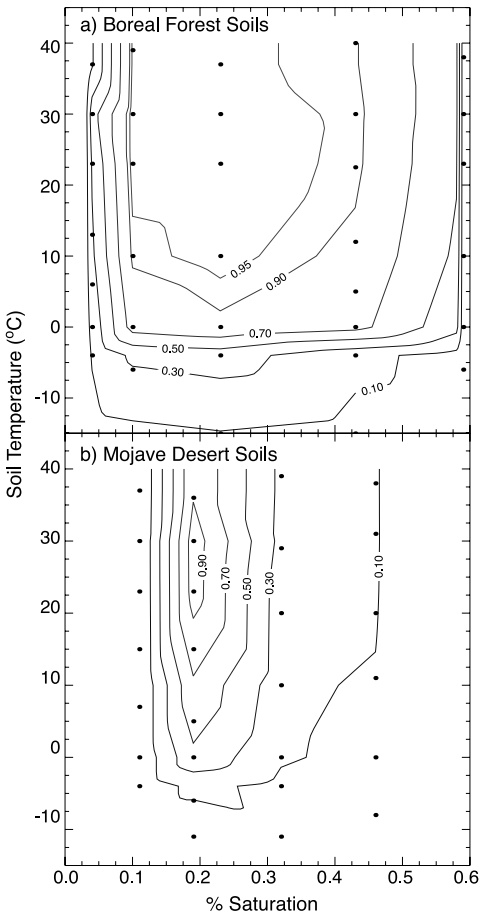

Figure 4. Contour plots of normalized uptake rate at each site as a function of temperature and moisture. Data were normalized by the maximum flux at each site. Grey dots represent locations of the data points used to generate the contour plots. (a) For boreal forest soils there was a relatively strong gradient between 0% and 10% saturation and −4°C and 0°C. (b) For Mojave Desert soils there was more symmetry about the moisture maximum as compared to the boreal forest soils. In constructing this plot, we assumed negative flux values measured in the Mojave Desert soils (Figure 3b) were equal to zero.

The low soil moisture inhibition of H_2 uptake has important implications for desert soils, and may lead to maximum H_2 uptake in wetter months despite the possibility of lower temperatures.

[19] The shape of the temperature and moisture response (Figure 4a) suggests that in boreal forest soils most of the variability in H_2 uptake by soils occurs under relatively low (−4°C to 15°C) temperatures and low soil moisture conditions. These observations may have important implications for the seasonal cycle of H_2 uptake globally. Northern soils routinely experience shifts in temperature over the range −4°C to 15°C seasonally. The timing of the spring drawdown of H_2, (beginning in May) and buildup (beginning in October) at northern latitudes [*Novelli et al.*, 1999] may be sensitive to the sharp increase in uptake that we observed between −4°C to 15°C (Figure S2). It is possible for northern soils to consume H_2 through the warmer parts of the winter, although the effect of snow cover, which may limit diffusion of H_2 into soils, must be measured and accounted for. Additionally, the seasonal and interannual soil moisture changes at these latitudes will affect the timing and magnitude of H_2 uptake.

[20] Boreal forest soil fluxes are approximately twice as large as Mojave Desert soil fluxes at the same temperature and soil moisture content. We hypothesize that this is due, in part, to differences in organic carbon content and soil structure. The two soils we examined have carbon contents near the extremes observed in common soils (0.02 to 38.5%) but more data is needed to clearly define the dependence of uptake on organic carbon content of soils. Although our laboratory measurements provided evidence that on a volumetric basis, boreal soils consume more H_2 than desert soils, chamber observations at these two locations do not show a large difference between surface flux rates per m^2 ground area [*Rahn et al.*, 2002] (N. Smith-Downey et al., manuscript in preparation, 2006). The net uptake at the surface is a product of the maximum uptake capacity of a soil (λ_{max}), the temperature and moisture controls defined here, along with the diffusion of H_2 into the soil profile. It is possible that despite a higher capacity for H_2 uptake per cm^3 soil, the boreal forest uptake is diffusion limited due to higher soil moisture or differences in soil structure. Constructing a model that takes all of these factors into account will allow us to examine sources of variability in the observed atmospheric H_2 record and to assess how climate change will influence future atmospheric levels of H_2.

[21] **Acknowledgments.** NSD thanks J. Leadbetter for lab and instrument use, K. Treseder for collecting soils in Alaska, X. Xu for assistance with the elemental analyzer, P. Ghosh, J. O'Leary, H. Afek and M. Child for help in the lab, and N. Downey. NSD received support from the NCER STAR program, EPA. JTR acknowledges support from UC Irvine's School of Physical Sciences Dean's Innovation Fund. This work was also supported by a generous gift from General Motors and William Davidow and family.

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